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**SEPARATING TEST ARTIFACTS FROM MATERIAL  
BEHAVIOR IN THE OXIDATION STUDIES OF HfB<sub>2</sub>-SiC  
AT 2000° C AND ABOVE (PREPRINT)**

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Separating Test Artifacts from Material Behavior in the Oxidation studies of  $\text{HfB}_2\text{-SiC}$  at 2000°C and above

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## **Abstract**

$\text{HfB}_2\text{-15 vol% SiC}$  prepared by field-assisted sintering was oxidized at 2000°C by heating in a zirconia-resistance furnace and by direct electrical resistance heating of the sample. The morphology and chemistry of the oxide scales were examined and compared. In addition, limitations of the materials and the direct electrical resistance heating apparatus were explored by heating samples multiple times and to temperatures in excess of 2300°C. Oxide scales that developed at 2000°C from both methods were similar in that they consisted of a  $\text{SiO}_2/\text{HfO}_2$  outer layer, a porous  $\text{HfO}_2$  layer, and a  $\text{HfB}_2$  layer depleted of SiC. But they were very different in scale thicknesses, impurities present, scale morphology/complexity. Possible test artifacts are discussed.

## **Keywords**

Oxidation, UHTC, Hafnium Diboride, Silicon Carbide

## **1. Introduction**

Characterization of the oxide scale formed on ultra high temperature ceramics (UHTCs) has been a topic of intense study over the past decade. In particular, composite systems of diborides of

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hafnium or zirconium with SiC have been studied for their improved oxidation resistance compared with the diborides alone near 1600°C [1-3]. At temperatures below 1800-2000°C, a refractory porous metal oxide scale is formed that is protected by a glassy silica scale. However, as temperatures are increased the protective silica becomes less viscous and thus less protective. Hypersonic flight at leading edges and nose cones will require that those components withstand rapid heating and cooling to temperatures in excess of 2000°C and shear from air flow [4,5]. These temperatures are unattainable in traditional molybdenum disilicide element furnaces, so new methods of testing have been developed. Methods such as oxyacetylene torch heating [6-8], laser heating [9], direct resistance heating of the sample itself [10-12], and scramjet simulators [13] are being developed. The rapid heating profiles and higher temperatures attainable with these tests may lead to different oxide morphologies and performance than observed with furnace heated samples. It is imperative that a correlation between different testing methods is made so that samples prepared by different exposure methods may be compared. To this end, HfB<sub>2</sub>-SiC samples were heated in air at 2000°C using a zirconia-resistance furnace and direct resistance heating of the sample and the resulting oxidation products were compared. Additionally, the limits of resistance heating including multiple cycles and maximum temperatures were examined.

## **2. Experimental Procedure**

Commercially available HfB<sub>2</sub> (Cerac ,99.9%, 45µm) and β-SiC (Cerac, 99.9%, 1µm) were used to prepare HfB<sub>2</sub>-15 vol% SiC (HS). The powder mixtures were ball milled in isopropanol for 24 h with SiC grinding media, dried at room temperature, and subsequently dry milled for 12 h. Typical weight loss of the SiC grinding media after milling was 0.2 mg (0.2 wt% of the total batch). The powders were sieved through an 80-mesh (177 µm) screen.

150 g of the milled powders were loaded into a 60-mm dia. graphite die. A layer of BN and graphite foil separated the powder from the die with the powder in contact with the graphite foil. The powder-filled dies were cold pressed at approximately 50 MPa. The powders were sintered

using field assisted sintering (FAS: FCT Systeme GmbH, Model HPD 25-1, Rauenstein Germany) at 2000°C for 15 min. under a 32 MPa load. The load was applied during heating to 1600°C and released on cooling to 1000°C. The controlled heating and cooling rates were 50°C/min. Oxidation samples were cut with a wire electro-discharge machine (EDM) into 5 x 5 x 3 mm<sup>3</sup> rectangles (furnace heating) and 53 x 3.5 x 5.0 mm<sup>3</sup> rectangles with a centered 19 to 25 mm long 3 mm thick region of reduced area (resistance heating). The samples were polished using diamond slurry to a 1-μm finish.

Polished samples were heated by a zirconia-resistance furnace (ZrF-25: Shinagawa Refractories Co., Tokyo Japan) and direct electrical resistance. Macrographs of the two tests and sample geometry are shown in Fig.1. The furnace heating was accomplished by a molybdenum disilicide pre-heater to 1100°C and a zirconia element to 2000°C at a rate of 5°C/min. The samples were held at temperature for 30 min. Samples were supported on a zirconia crucible. The zirconia crucibles were cut from a larger crucible (Advalue Tuscon, AZ; 10-mL Ca-stabilized ZrO<sub>2</sub> crucible; 95% ZrO<sub>2</sub> and 4±1% Ca). Direct electrical resistance heating was controlled by the power output of an AC power supply across the sample and temperature was read by a 2-color pyrometer (FMP2, FAR Associates, Macedonia, OH) that was focused on the center of the reduced-thickness area. Temperature, current, and voltage data were recorded using LabVIEW (National Instruments, Austin TX). Table 1 lists the oxidized samples with their heating conditions. Oxidized samples were mounted in epoxy and polished in cross-section perpendicular to the bottom (side facing the crucible or notched side) of the sample to a 1-μm finish using diamond slurry. The microstructures were characterized using scanning electron microscopy (SEM: Quanta, FEI, Hillsborough, OR) along with energy dispersive spectroscopy (EDS: Pegasus 4000, EDAX, Mahwah, NJ) for elemental analysis. All EDS analysis was done using 15 kV accelerating voltage and at least a 100 s live capture time.

### 3. Results

#### 3.1 Single 2000°C Exposure

The heating profiles of the  $\text{HfB}_2$ -15 vol% SiC zirconia-resistance furnace heated sample (HS-F) and direct electrical resistance heated (HS-R) sample are shown in Fig. 2a and Fig. 2b, respectively. The maximum observed temperature of the HS-R sample was 2027°C using 82.5 V and 20.3 A (averaged over the hold). The oxidized HS-F sample had a thicker oxide scale (Fig. 3a) compared to the HS-R sample (Fig. 3b). The HS-F sample was exposed to oxidizing temperatures for a greater length of time than the HS-R sample (6.5 h above 1100°C compared to approx. 4 min above 800°C). The oxide layers labeled in Fig. 3a (HS-F) and Fig. 3b (HS-R) are composed of (I) a  $\text{SiO}_2$ -based glass that penetrates a  $\text{HfO}_2$ -based skeleton; (II) a porous  $\text{HfO}_2$  scale; and (III) a SiC depleted layer. The SiC-depleted layer is defined as  $\text{HfB}_2$  with a reduced SiC content (partially oxidized SiC). The average total oxide scale thickness measured from the top side of the HS-F sample is 661  $\mu\text{m}$  with the depleted layer comprising 53% of the scale. The thickest total oxide scale measured on the HS-R sample was 105  $\mu\text{m}$  with 5% of the total scale consisting of the depleted layer.

The oxide scales of HS-F samples possess a distinct 2-phase  $\text{SiO}_2$ -based glass with the less-pure (less viscous) impurity laden glass rising to the surface of the oxide scale and the purer glass found deeper within the scale (Fig. 4a). A 2-phase glass found in furnace heating has been described previously by the authors, which was shown to contain Al and Ca as major impurities [14]. Additionally,  $\text{HfSiO}_4$  (with a Ca impurity) is found in the HS-F sample, but not the HS-R sample. The existence and absence of  $\text{HfSiO}_4$  was confirmed by XRD. Figure 4b is an EDS comparison of the purer (darker) and impure (lighter) glasses in the HS-F sample along with the  $\text{HfSiO}_4$  and  $\text{HfO}_2$  phases. In the HS-R sample Al impurities can be found randomly distributed throughout the glassy phase (inset Fig. 4c). Figure 4d is a representative EDS spectra of different locations within the HS-R glass. There is no hierarchy to the concentration of Al in the glass phase when comparing the chemistry of the glass along the length of the HS-R oxide scale.

### 3.2 Repeated 2000°C exposure

An advantage of the direct electrical resistance heating test is that the sample can be exposed multiple times to the same or different heating profiles. A sample (HS-Rr) was heated to 2000°C twice using the same heating profile as HS-R. The maximum observed temperature was 2030°C. The heating profile and a micrograph of the resulting oxide scale are shown in Figs. 5 a and b. The oxide scale has a periodic structure consisting of layers of  $\text{SiO}_2$  and  $\text{HfO}_2$  penetrated by  $\text{SiO}_2$ . For comparison, a sample (HS-R2) was heated to 2000°C for two min. (Fig. 5c) with a maximum observed temperature of 2040°C. The oxide scale thickness of the HS-R2 sample was double that found for the HS-R sample (217  $\mu\text{m}$  vs. 105  $\mu\text{m}$ ), and the oxide scale was not composed of periodic layers. The oxide scale formed near the center of the reduced area on the HS-Rr and HS-R2 samples were non-adherent. Cracks were also observed within the depleted layer of the HS-F sample and at the interface between  $\text{HfO}_2$  and the SiC-depleted layer (Fig. 3a). In the HS-R sample fracture is observed between the depleted layer and the  $\text{HfO}_2$  layer at the center of the sample (Fig. 3b), while adherent oxide scales exist near the end of the reduced area.

### 3.3 Temperatures beyond 2000°C

The maximum temperature of the direct resistance test is limited only by the available power and the survivability of the sample. A sample (HS-Rf) was heated to failure, where failure was defined as the sample fracturing such that the electrical path was disrupted. The maximum observed temperature was 2325°C. A micrograph of the cross section of the HS-Rf sample (Fig. 6) reveals extensive internal damage. Large pores are found inside the sample while an oxide scale covers the surface. The bulk unoxidized material from the center of the sample (inset Fig. 6) was confirmed by EDS to be SiC and  $\text{HfB}_2$ . The microstructure suggests formation of a liquid phase, which is consistent with the calculated eutectic at 2347°C in the  $\text{HfB}_2$ -SiC system [15]. The oxide scale (inset Fig. 6) is composed of  $\text{HfO}_2$  penetrated by  $\text{SiO}_2$ . Meng et. al. [12] similarly showed the

failure of a  $\text{ZrB}_2\text{-SiC}$  sample at temperatures above  $2300^\circ\text{C}$  ( $2207^\circ\text{C}$  eutectic temperature [15]), but did not show any micrographs of the interior microstructure.

#### 4. Discussion

The direct comparison of the zirconia-resistance heated and direct-electrical resistance heated  $\text{HfB}_2\text{-SiC}$  samples at  $2000^\circ\text{C}$  provide insight to the limitations of furnace heating. Due to slower heating rates and contamination from contact between the sample and crucible, the HS-F total oxide scale thickness is greater than observed in the HS-R sample. The difference in heating rates can also explain the observation of  $\text{HfSiO}_4$  in the HS-F sample and not in the HS-R sample.

$\text{HfSiO}_4$  is only stable below  $\sim 1726^\circ\text{C}$  [16,17], therefore; its formation in the HS-F sample could occur during slow cooling.  $\text{HfO}_2$  and  $\text{SiO}_2$  form an incongruently melting silicate and thus require solid-state diffusion to form the silicate phase adding an extra kinetic limitation on its formation [16]. The rapid heating and cooling rates of the HS-F sample presumably do not allow for the separation of glasses with different viscosities or for the formation of  $\text{HfSiO}_4$ .

Additionally, the lack of Ca impurity in the resistance-heated sample suggests the source of the impurity to be the zirconia crucible or zirconia heating element, while the presence of Al in both samples implies it is an inherent impurity in the starting powders. The  $\text{HfB}_2$  and  $\text{SiC}$  powders are reported by the manufacturer to contain 0.03% and 0.01% Al respectively. Figure 7 is a micrograph showing the  $\text{SiC}$  grains with a pocket of impurities in the as-processed material. These areas can be found throughout the sample adjacent to  $\text{SiC}$  grains and are shown by EDS (inset) to contain Si, Al, and O. The slow heating rates and contact contamination issues of the zirconia-element furnace are not expected in hypersonic flight conditions and serve to complicate the analysis of UHTC oxidation resistance testing.

When an  $\text{HfB}_2\text{-SiC}$  sample is heated by direct-electrical resistance through multiple heating and cooling cycles spallation of the oxide scale is suggested by the presence of the repeating  $\text{SiO}_2\text{-HfO}_2$  layers. Such layered oxide structures have not been reported for furnace heated samples and was not observed in a sample heated for the same time (HS-R2) but that only experience a



single heating and cooling cycle. There are two sources of stress during oxidation that may lead to fracture during temperature changes: (1) thermal expansion mismatch and (2) volume changes associated with phase transformations. The coefficient of thermal expansion (CTE) of  $\text{HfO}_2$  depends on the impurity content and phase, but typical values are  $5 \cdot 10^{-6}$  to  $7 \cdot 10^{-6} \text{ K}^{-1}$  for room temperature to  $1250^\circ\text{C}$  with purer  $\text{HfO}_2$  having lower values [18,19]. Gasch et al. [20] measured the CTE of pure  $\text{HfB}_2$ , pure  $\text{SiC}$ , and a combination of  $\text{HfB}_2$ -20vol%  $\text{SiC}$  to find that the CTE of  $\text{HfB}_2$ -20vol%  $\text{SiC}$  was  $\sim 5 \cdot 10^{-6} \text{ K}^{-1}$  at room temperature and  $\sim 7 \cdot 10^{-6} \text{ K}^{-1}$  at  $1600^\circ\text{C}$  and fell between the CTE values of pure  $\text{HfB}_2$  (higher) and  $\text{SiC}$  (lower) as expected by the rule of mixtures. The reported CTE values for  $\text{HfO}_2$  and  $\text{HfB}_2$ - $\text{SiC}$  are presumably not different enough to cause cracking due to thermal expansion mismatch. Additionally, the slow cooling rate ( $5^\circ\text{C}/\text{min}$ ) in the furnace heated samples is not likely to introduce a thermal shock necessary to produce cracking in the sample. The transformation of  $\text{HfO}_2$  from monoclinic to tetragonal upon heating (10% conversion at  $1642^\circ\text{C}$ ) or tetragonal to monoclinic during cooling (10% conversion at  $1710^\circ\text{C}$ ) [17,21,22], is accompanied by a 3 to 3.5% volume contraction/expansion upon heating/cooling [21,23]. This volume expansion could lead spallation of the oxide scale. The multiple layers found in the HS-RR sample and gradient from non-adherent to adherent oxide scales along the length (temperature profile) in all the samples heated by direct electrical resistance offer indirect evidence that the phase transformation can promote spallation. The role of CTE mismatch and  $\text{HfO}_2$  phase transformation on oxide scale adherence deserve further study.

The limitation of the resistance heater was explored as the sample was heated to failure above  $2300^\circ\text{C}$ . The entire sample was soaked at the elevated temperature allowing for the formation of the  $\text{HfB}_2$ - $\text{SiO}_2$  liquid phase inside of the HS-Rf sample. Furthermore, the temperature may be greater in the interior because the oxide scale will not be electrically conductive and is an effective thermal insulator. The higher electrical resistivity of  $\text{SiC}$ , could promote a favored heating of this phase over the  $\text{HfB}_2$  allowing it to approach its melting temperature ( $\sim 2700^\circ\text{C}$ ). Under flight

conditions, only the outer regions of the sample would be heated and the electrical resistance of the two phases would not be a factor.

## **5. Conclusion**

Temperatures up to 2000°C can be achieved in a laboratory furnace; however, these tests suffer from slow heating profiles and potential interactions between furnace materials and the sample being tested. The observation of Ca and HfSiO<sub>4</sub> in the oxide scale affects the glass properties, but is not realistically expected in a flight environment. The use of resistance heating allows non-contact testing with a high heating profile. Features like fracture between the oxide scale and the depleted layer and Al impurities are universal observations between both heating tests and require further investigation. Additionally, research to stabilize the tetragonal transformation may aid in a more adherent scale. Resistance heating may be further utilized to study multiple heating profiles and test materials for scale adherence. The resistance testing is limited by the uniform heating of the sample that would not be expected in a real flight environment. Further comparison of test methods such as laser heating, oxyacetylene torch testing, or scramjet testing would be beneficial to understanding material properties.

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**Fig. 1.** (a) Macrograph of direct-electrical resistance heating apparatus showing the copper electrodes and a heated sample gripped by carbon spacers. The pyrometer is read by means of a fiber optic cable through a carbon tube. (b) Macrograph of the zirconia-resistance furnace showing the (A) sample stand (B) cylindrical zirconia heating element, (C) alumina insulation, and (D) molybdenum oxide insulation. (c) Samples prepared for direct electrical heating (top) and zirconia-resistance heating (bottom) on the supporting zirconia crucible. The Ag paste improves electrical conduction.

**Fig. 2.** Heating profiles of the (a) HS-F (calculated) and (b) HS-R (actual) samples.

**Fig. 3.** (a) Micrograph of the HS-F sample after oxidation at 2000°C (b) Micrograph of the HS-R sample after oxidation at ~2000°C. The oxide layers are (I) HfO<sub>2</sub> penetrated by SiO<sub>2</sub>, (II) porous HfO<sub>2</sub>, and (III) depleted HfB<sub>2</sub> layer.

**Fig. 4.** (a) Micrograph showing the different phases found in the HS-F oxide scale (1) SiO<sub>2</sub>, (2) Si-Al-O, (3) HfSiO<sub>4</sub> with Ca, and (4) HfO<sub>2</sub>. (b) EDS corresponding to the phases found in (a). (c) Micrograph showing the HfO<sub>2</sub> (light) and Si-O-Al (dark) phases found in the HS-R oxide scale (d) EDS of the Si-Al-O phase corresponding to (c). In the EDS spectra \*Al, ^Ca, +Si, #Hf, &O, ~C.

**Fig. 5.** (a) Heating profile of sample HS-Rr. (b) Micrograph of the oxide found in hottest region of the oxidized HS-Rr sample heated to 2000°C for one minute two times. (c) Micrograph of the oxide found in hottest region of the oxidized HS-R2 sample heated to 2000°C for two minutes. The layers are the same as those found in the HS-R sample: (I) HfO<sub>2</sub> penetrated by SiO<sub>2</sub>, (II) porous HfO<sub>2</sub>, and (III) depleted HfB<sub>2</sub>.

**Fig. 6.** Micrograph of the HS-Rf sample heated to 2325°C. The white-outlined inset is the transformed SiC (dark)-HfB<sub>2</sub> (light) structure found in the interior of the sample. The black-outlined inset is the oxide scale composed of HfO<sub>2</sub> and SiO<sub>2</sub> found on the exterior of the HS-Rf sample.

**Fig. 7.** Micrograph showing a Si-Al-O impurity phase in the bulk of the HfB<sub>2</sub>-15 vol%SiC sample. The C signal in the EDS (inset) is from the carbon coating applied to the sample.

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Table 1. List of the oxidized HfB<sub>2</sub>-15 vol% SiC samples and their heating conditions

Sample ID	Test Method	Max. Observed Temp. (°C)	Hold Time (min.)	Comments
HS-F	Furnace	2000	30	-
HS-R	Self-Heating	2027	1	-
HS-Rr	Self-Heating	2030	1	Two 1 min. holds
HS-R2	Self-Heating	2041	2	-
HS-Rf	Self-Heating	2325	0	Heated to failure